



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of Katsuhiko NAMBA et al.

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Examiner : THORNTON, YVETTE C.

CHEMICAL AMPLIFYING TYPE POSITIVE RESIST
COMPOSITION

* * * * *

DECLARATION

I, Junji NAKANISHI, residing at 5-1,
Otowayakude-cho, Yamashina-ku, Kyoto-shi, Kyoto, 607-8076,
Japan, declare and say:

that I graduated and obtained Master Degree from Graduate School
of Engineering, Osaka Prefecture University in March 1999.

Since April 1999 to the present, I have been employed by
Sumitomo Chemical Co., Ltd., assignee of the above-identified
application, and engaged in research and development in the field of
syntheses of resins and of product developments for photoresist
compositions;

that I am one of the inventors of the invention of the
above-identified application; and

that in order to examine whether the relativity of the flexibility imparting effect on a film and the preventing effect on scum production is present or not, I beg to submit the following experimental data which have been obtained under my supervision:

Experiments

1. MATERIALS

(1) Resins

i) Resin A1

Resin A1 was synthesized according to the method described in the present specification “(1a) Synthesis of copolymer of 2-ethyl-2-adamantyl methacrylate and p-acetoxystyrene (20:80)” and “(1b) Synthesis of copolymer of 2-ethyl-2-adamantyl methacrylate and p-hydroxystyrene (20:80)” from page 14, line 4 to page 15, line 11.

Resin A1 had a weight-average molecular weight (M_w) of about 8400 and a degree of dispersion of 1.7 (GPC method: in terms of polystyrene), and revealed a copolymerization ratio of about 18:82 measured by a nuclear magnetic resonance (^{13}C -NMR) spectrometer.

ii) Resin B1

Resin B1 was synthesized according to the method described in the present specification “(2a) Synthesis of copolymer of 2-ethyl-2-adamantyl methacrylate and p-acetoxystyrene (30:70)” and “(2b) Synthesis of copolymer of

2-ethyl-2-adamantyl methacrylate and p-hydroxystyrene (30:70)” from page 15, line 12 to page 16, line 18.

The resin had a weight-average molecular weight (M_w) of about 7800 and a degree of dispersion of 1.8 (GPC method: in terms of polystyrene), and revealed a copolymerization ratio of about 29:71 measured by a nuclear magnetic resonance (^{13}C -NMR) spectrometer.

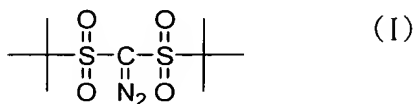
(2) Component X

Among the examples of the plasticizer, at column 35, lines 11-16 in Nakamura et al., the following compounds are selected as Compound X based on the criteria of their commercial availability.

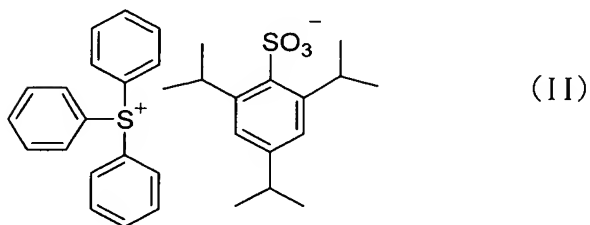
- (a) polypropylene glycol (M_w : about 2000) (in Example 1)
- (b) polyacrylic acid (M_w : about 2000) (in Comparative Example 1)
- (c) tri-n-butyl citrate (in Comparative Example 2)
- (d) diethyl phthalate (in Comparative Example 3)
- (e) di-n-butyl phthalate (in Comparative Example 4)
- (f) di-n-hexyl phthalate (in Comparative Example 5)
- (g) di(2-ethylhexyl) phosphate (in Comparative Example 6)
- (h) tri-n-butyl phosphate (in Comparative Example 7)
- (j) tricresyl phosphate (in Comparative Example 8)
- (k) tris(2-ethylhexyl) phosphate (in Comparative Example 9)
- (l) none (in Comparative Example 10)

(3) Acid generating agents

i) Acid generating agent I of the following formula (I)



ii) Acid generating agent II of the following formula (II)



(4) Quencher

diisopropylaniline

(5) Solvent

propylene glycol monomethyl ether acetate

2. Examples and Comparative Examples

(1) Preparation of Resist Composition

Resin A1 and Resin B1 was mixed at a ratio of 1:1 to give a resin mixture, and 13.5 parts by weight of this resin mixture was mixed with 0.45 part of Acid generating agent (I) and 0.45 part by weight of Acid generating agent (II), 0.055 part by weight of quencher and 90 parts by weight of solvent to provide a solution. This solution was further filtrated through a fluorine resin filter having

a pore diameter of 0.2 μm to prepare a resist solution.

To this resist solution was added Component X shown above in an amount of 1% based on the resin mixture to obtain resist solution containing Component X.

(2) Evaluation of Resist Solution

On a silicon wafer, an anti-reflection film [“DUV-42” manufactured by Nissan Chemical Industries. Ltd.] was applied under pre-bake conditions of 215 °C and 60 seconds to give a thickness of 0.06 μm . Then, each of the resist solution containing Component X was spin-coated on this, followed by pre-baking on a proximity hot plate under conditions of 110°C and 60 seconds to form a resist film having a thickness of 0.42 μm . A wafer carrying thus formed resist film was exposed using a KrF excimer stepper [“NSR-2205EX12B” manufactured by Nikon Corp., NA=0.55, σ =0.80, 2/3 annular illumination] via masks having various forms and dimensions. Then, PEB was conducted under conditions of 130°C and 60 seconds on a hot plate, further, puddle development was conducted for 60 seconds with a 2.38% tetramethyl ammonium hydroxide aqueous solution. Patterns after development were observed by a scanning electron microscope, and sensitivity, resolution and presence of scum were checked as described below. Results are shown in Table 1.

Film penetrating sensitivity: This was indicated by the minimum exposure required for film penetration of 2 mm square open field after exposure

and development. This is represented by Eth.

Effective sensitivity: This was indicated by exposure amount at which 0.20 μm line and space pattern was 1:1. This is represented by Eo.

Presence of scum: A wafer carrying patterns formed at exposure at which 0.20 μm line and space pattern was 1:1 was observed from the upper surface using a scanning electron microscope, and presence of scum (residue) at exposed parts was checked. Observation of one or more scum was represented by \times , and observation of no scum was represented by \bigcirc .

Resolution: This was indicated by the minimum dimension of line and space pattern separating at exposure of effective sensitivity.

Table 1

Example No.	Component X	Sensitivity		Resolution (mm)	Presence of scum
		(mJ/cm ₂)			
		Eth	Eo		
Exp. 1	(a)	12	32	0.18	○
Comp.Exp.1	(b)	Unable to evaluate*			
Comp.Exp.2	(c)	12	31	0.18	×
Comp.Exp.3	(d)	12	32	0.18	×
Comp.Exp.4	(e)	12	33	0.18	×
Comp.Exp.5	(f)	12	32	0.18	○
Comp.Exp.6	(g)	12	28	0.19	×
Comp.Exp.7	(h)	12	31	0.18	×
Comp.Exp.8	(j)	12	32	0.18	×
Comp.Exp.9	(k)	12	31	0.18	×
Comp.Exp.10	(l)	12	32	0.18	×

*:Unable to evaluate due to the insolubility of Component X in the solvent

3. Discussions and Conclusions

Exp. 1 corresponds to the present invention and contains polypropylene glycol. Comp.Exp. 10 contains no Component X. Apparent from the comparison of the results of Exp. 1 and Comp.Exp. 10, the present invention has a great preventing effect on scum production.

On the other hand, Comp.Exp. 1 to 4, 6 to 9 do not have such preventing effect on scum production, and only Comp.Exp. 5 containing di-n-hexyl phthalate does have.

From the results of Comp.Exp. 1 to 9 above, I can conclude that the flexibility imparting effect on a film and the preventing effect on scum production are totally different and that no relativity exist therebetween.

I declare further that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United State Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Signed this 24th day of June 2004.


Junji NAKANISHI